# Materials Modeling for Rocket Propulsion

OSC Workshop on Materials Modeling for National Security

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This briefing contains information up to:

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# Outline

**1. Introduction**

**2. Technical challenges in propellant design**

**3. Modeling and Simulation (M&S) techniques & tools**

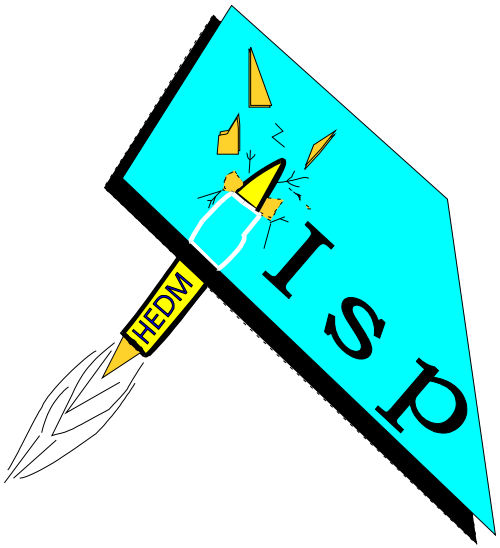
a) Quantum chemistry
b) Molecular dynamics
c) QSPR
d) High Performance Computing (HPC)

**4. Examples**

a) Identification of suitable target compounds
b) Determination of viable intermediates
c) Confirmation of successful synthesis

**5. Summary and Conclusions**

# 1. What We Are Doing

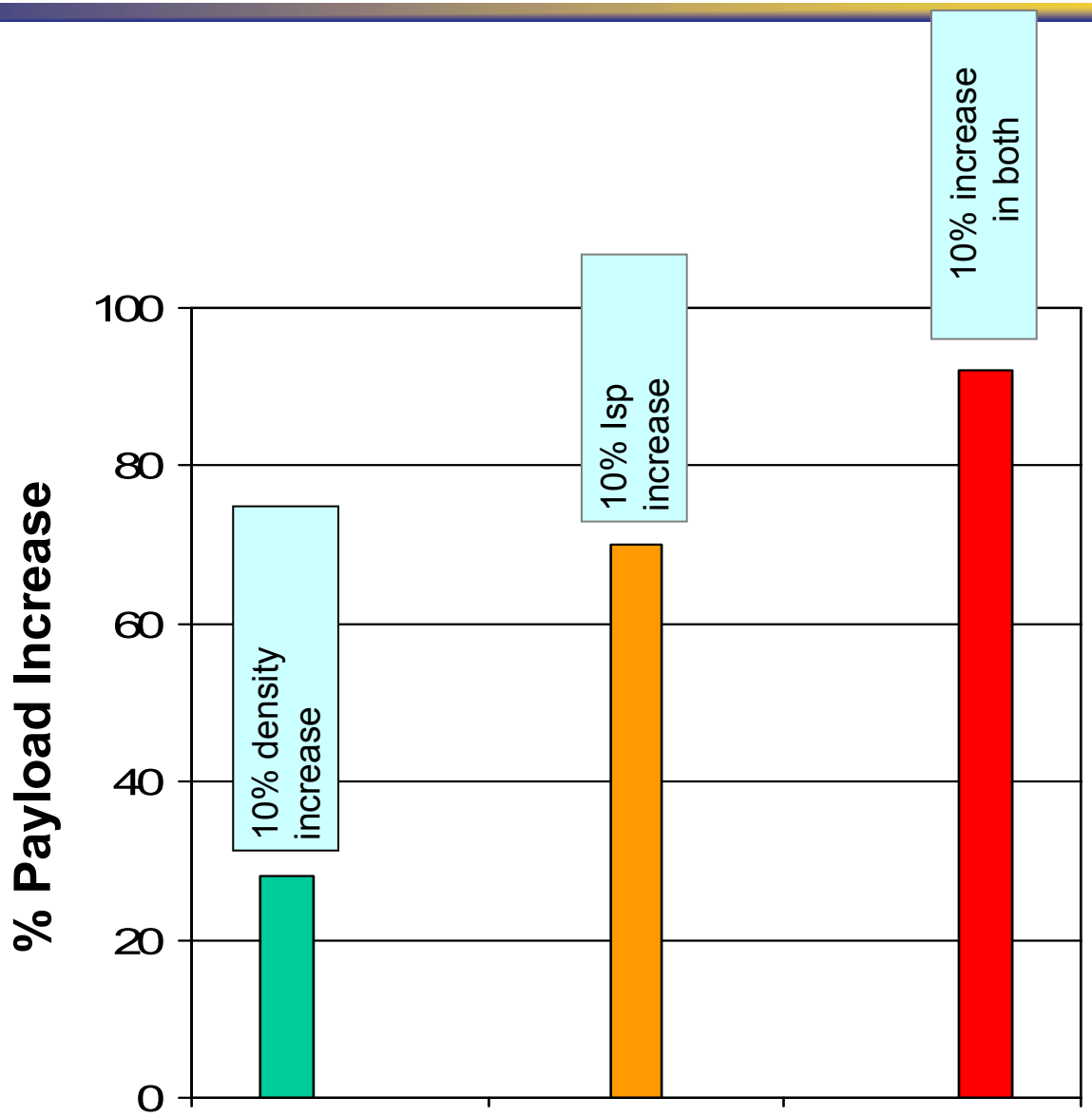



*Breaking the performance barrier*

**Identifying and developing advanced chemical propellants for rocket propulsion applications**

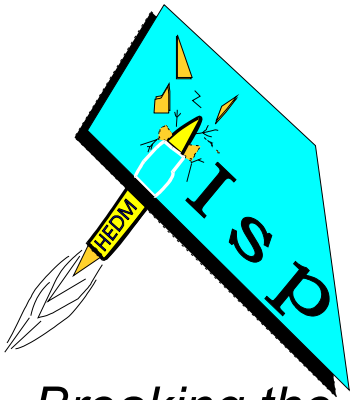
- **Isp is the major metric of a propellant's performance**
- **Density can also be a significant contributor**

# 1. Why We Are Doing It



# 1. How We Do it

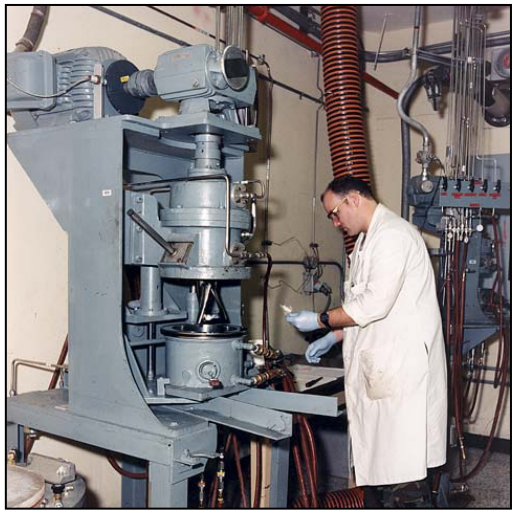
## High Energy Density Matter




*Breaking the performance barrier*

- Advanced solid ingredients
- Computational Chemistry
- Polynitrogen chemistry
- Ionic liquids
- Advanced hydrocarbon fuels
- Ignition studies

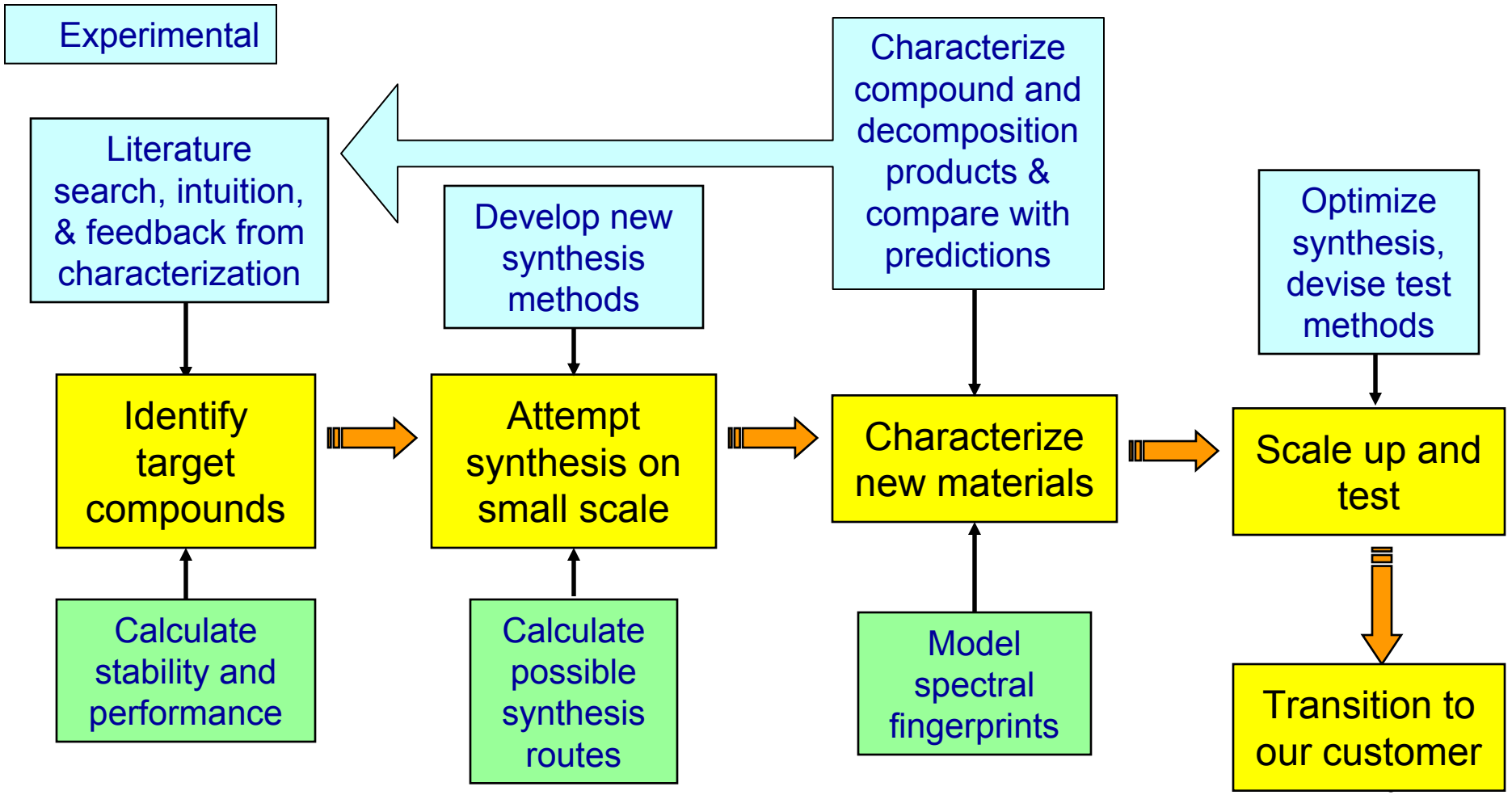
## Propellant Development



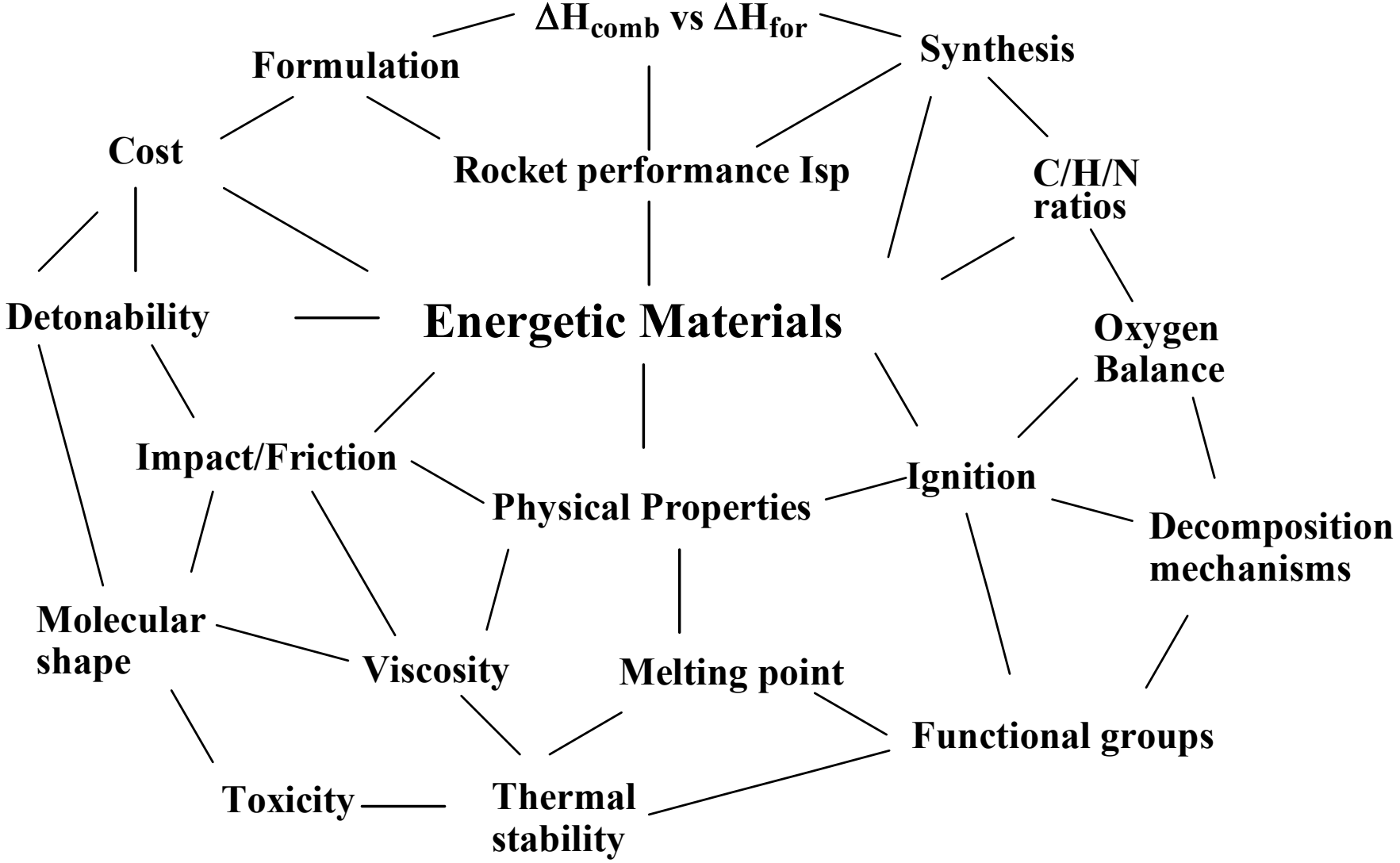
- Ingredient characterization
- Propellant characterization
- Ingredient scale up
- Propellant scale up
- Small scale hot fire propellant testing

# 1. Propellants Program General Approach

Employ a synergic blend of experimental (synthesis and physical) and computational techniques derived from the disciplines of chemistry and physics



# 2. Challenges in Propellant Design



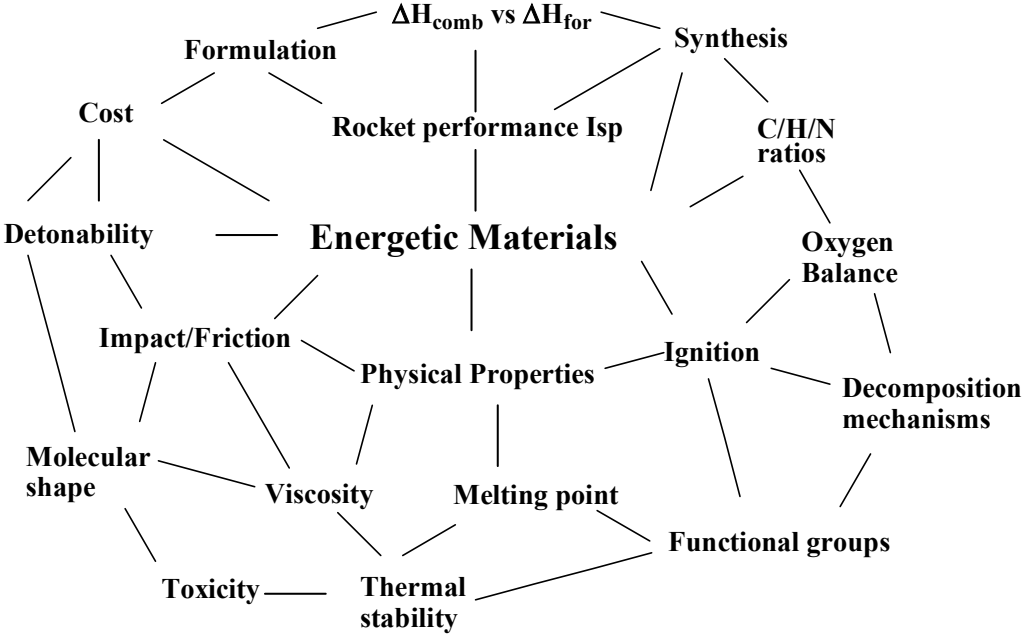
# 2. Challenges Addressed by M&S

**Stability**

**Energy Content**

**Reactivity**

- Synthesis
- Ignition
- Combustion
- Decomposition




**Bulk properties**

- Melting points
- Densities
- Transport properties (e.g., thermal conductivity)

**Sensitivity (impact/friction/shock)**

**Toxicity**

# 3. M&S of New Chemical Propellants: Quantum Chemistry

Various computational techniques are employed to solve the molecular electronic Schrödinger equation (SE) from quantum mechanics:

$$\left[ -\frac{1}{2}\sum_i \nabla_i^2 - \sum_i \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} + \sum_i \sum_{j>i} \frac{1}{r_{ij}} \right] \Psi_{el} = E_{el} \Psi_{el}$$

**Is a proposed propellant molecule/energetic material stable?**

- **Structure optimization, verification as local minimum**

**What is its energy content?**

- **Heat of formation**

**How may it be synthesized? How will it react/decompose/combust?**

- **Reaction pathways**

**How will we know if we've synthesized it?**

- **Vibrational spectra (IR, Raman, isotopic shifts)**
- **NMR chemical shifts**
- **Electronic spectra**

# 3. M&S of New Chemical Propellants: Molecular Dynamics

Classical Equations of motion solved to simulate and predict various properties

$$\vec{F} = m\vec{a}$$

**Bulk properties**

Phase transitions (esp. melting points), densities, transport properties

**Processes affecting sensitivity**

Shock wave propagation vs. dissipation, energy transfer

# 3. M&S of New Chemical Propellants: QSPR

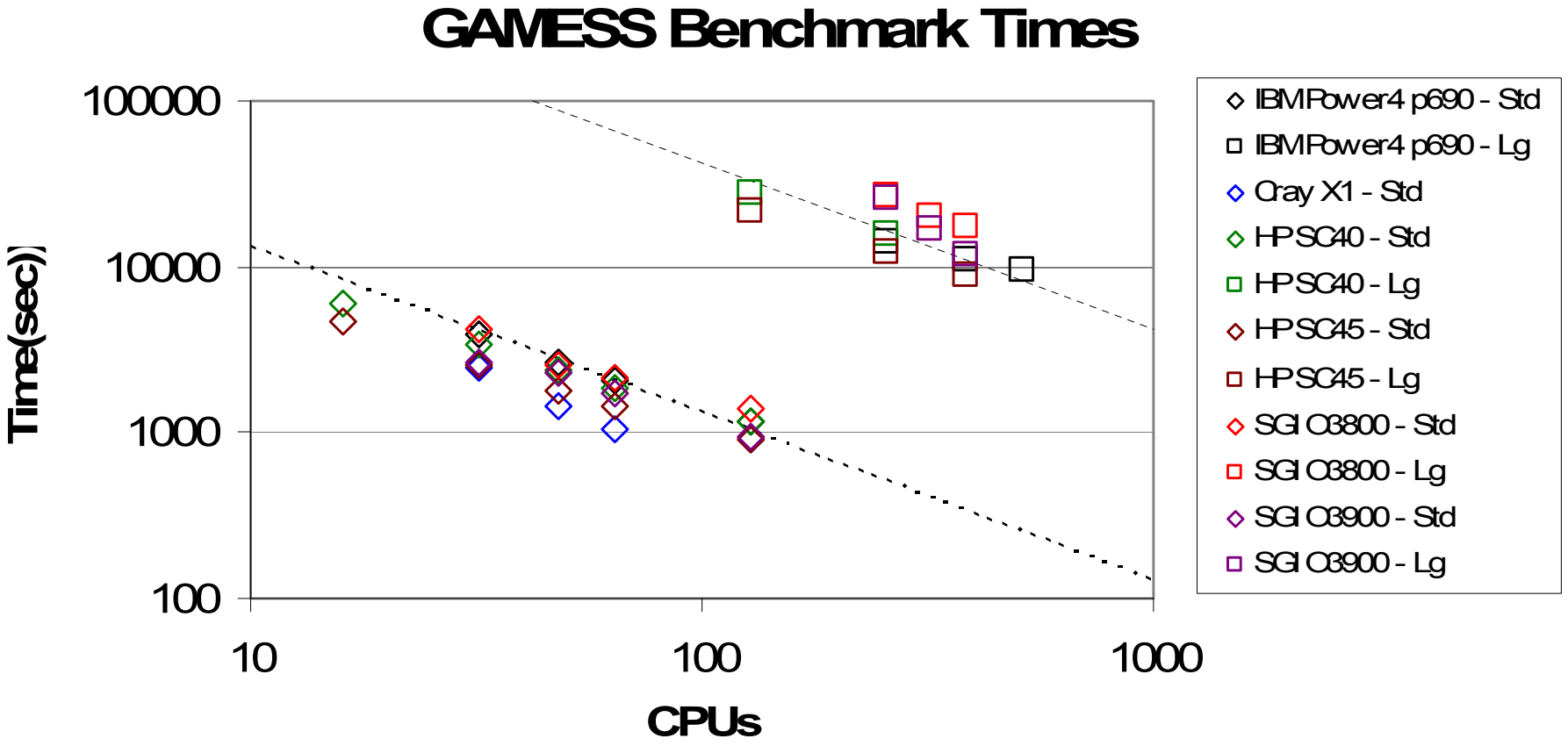
Derivation of empirical expressions relating molecular descriptors to key properties

**Bulk Properties**

**Sensitivity**

**Toxicity**

# 3. M&S of New Chemical Propellants: High Performance Computing



# 3. HPC Tools

Software: A variety of computer programs are used to perform the quantum chemical calculations, including:

- **GAMESS (General Atomic and Molecular Electronic Structure System), from Iowa State University (Mark Gordon et al.)**
- **ACES II (Advanced Concepts in Electronic Structure), from University of Florida (Rod Bartlett et al.)**
- **GAUSSIAN 98, from Gaussian, Inc. (John Pople et al.)**
- **MOLPRO 98, from University of Birmingham (UK)**

Hardware: A variety of scalable computing systems (IBM SP/Px, Cray T3E, SGI Origin, Linux clusters, etc.) at the DoD HPC centers, plus local computing resources.

# 4. Examples

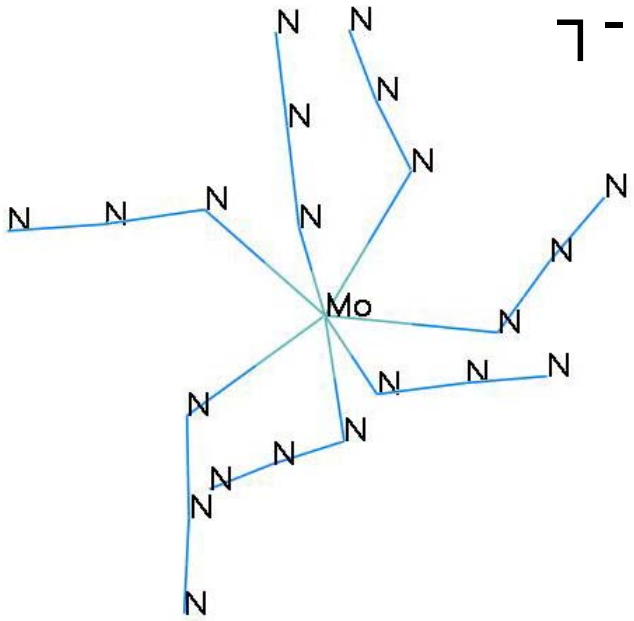
**The AFRL-Edwards (PRSP) theory/computational group supports several in-house experimental programs:**

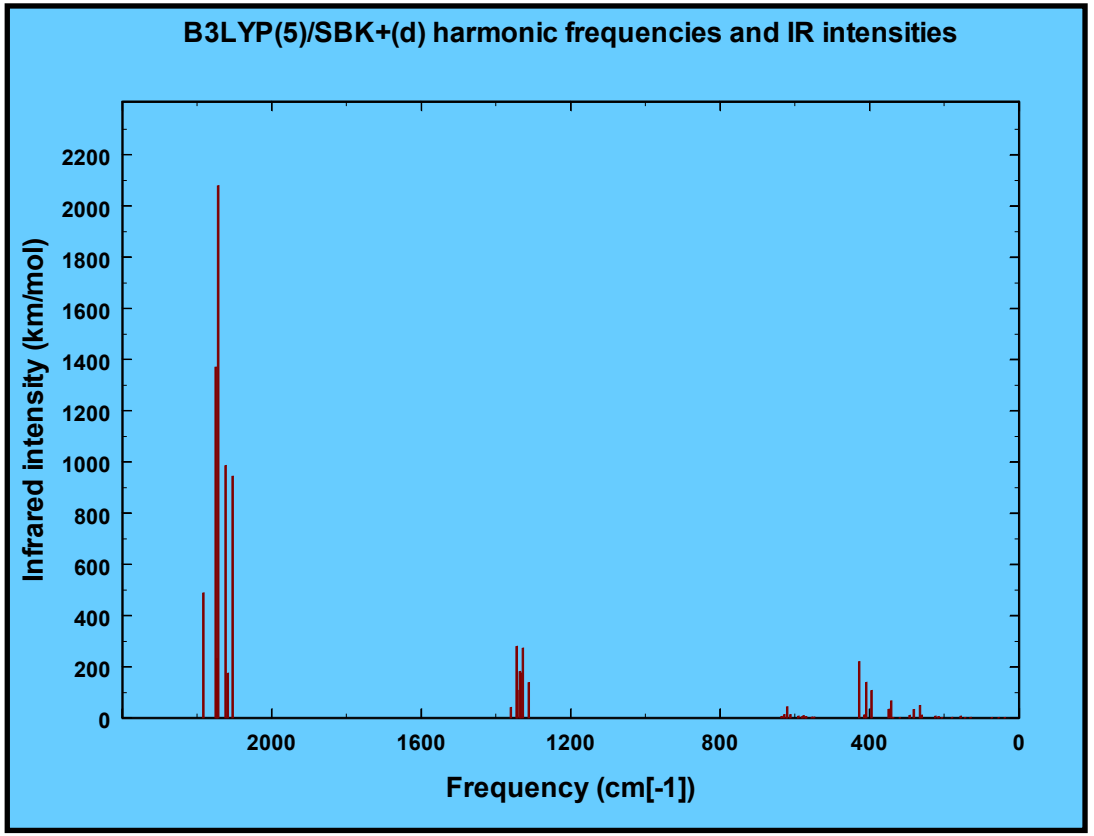
- **a) Polynitrogen/high nitrogen chemistry**
- **b) Energetic ionic liquids**
- **b) Ionic liquids ignition/combustion**
- **c) Energetic hydrocarbons**
- **d) Energetic solid ingredients**

# 4. New Polynitrogens/High Nitrogen Compounds: Identifying Intermediates

**Role of theory and computation:** We calculate the structures, infrared and Raman vibrational spectra, and isotopic vibrational shifts.

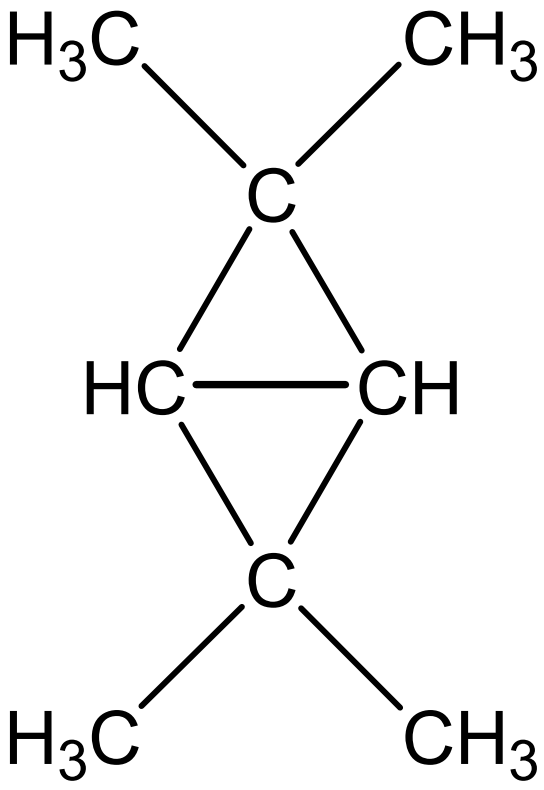
$[Mo(N_3)_7]^-$



# 4. Energetic Hydrocarbons: Identifying Target Compounds

**Role of theory and computation:** We calculate the structures, vibrational spectra, heats of formation, and Isp of new hydrocarbons



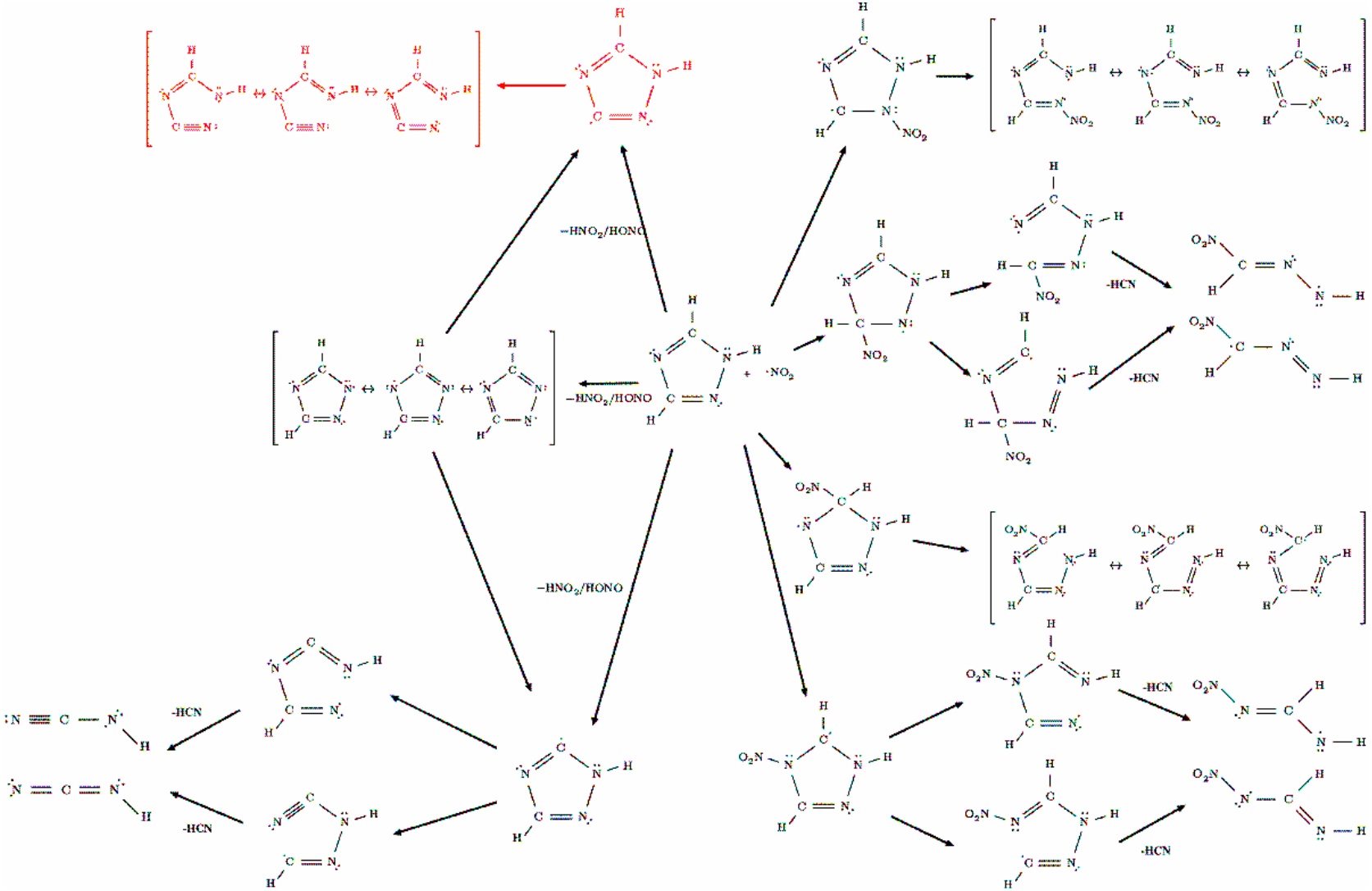

2,2,4,4-tetramethylbicyclo[1.1.0]butane

Potential payoffs of advanced hydrocarbons

- Enabling new missions – up to 30% more payload on launch vehicles
- Cutting payload-to-orbit costs – 15% reduction for current expendable rockets; 90% reduction if incorporated into next-generation reusables

$\Delta H_f$ = 0.285 kcal/g

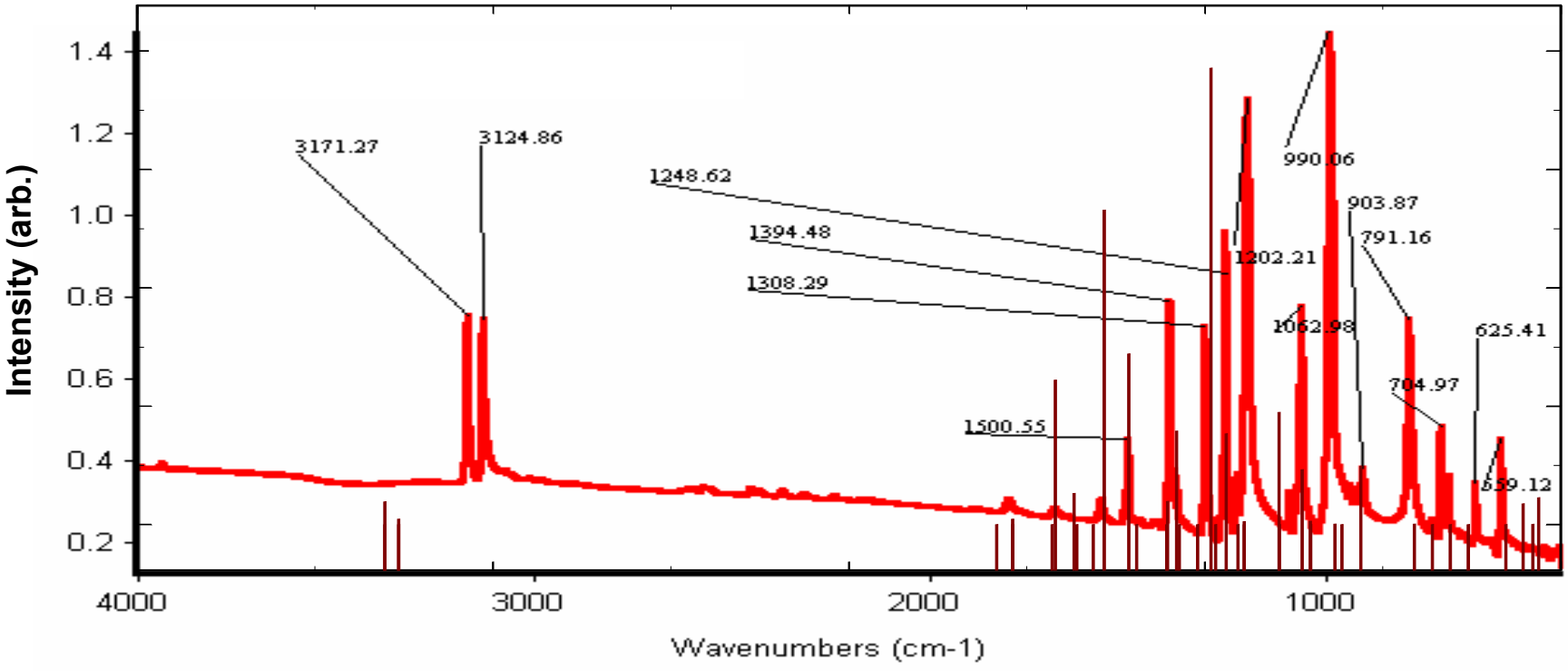
# 4. Hypergolic Ignition Modeling



# 4. Energetic Solid Ingredients: Confirmation of Successful Synthesis

**Role of theory and computation:** We calculate the structures, infrared and Raman vibrational spectra, and isotopic vibrational shifts.

**Comparison of calculated (B3LYP(5)/6-311G(d,p)) and experimental infrared vibrational spectrum.**



# 5. Collaborators

Dr. Jeff Mills (AFRL/PRSP) – ignition studies, QSPR, ionic liquids, hydrocarbons, ….

- **Extramural collaborations**

  Spectral Theory: Prof. Peter Langhoff (**San Diego Supercomputing Center**), Prof. R.J. Hinde (**Univ. of Tennessee-Knoxville**), Dr. Jeff Sheehy (**NASA MSFC**).

  Solid Ingredients: Prof. Don Thompson (**University of Missouri-Columbia**), Dr.Dan Sorescu (**USDOE National Renewable Energy Laboratory**)

  Ionic Liquids: Prof. Mark Gordon (**Iowa State University**), Prof. Greg Voth (**Univ. of Utah**), Prof. Sharon Hammes-Schiffer (**Univ. of Penn**.), Dr. Ruth Pachter (**AFRL/ML**).

  Hydrocarbons: Dr. Mike Zehe (**NASA GRC**)

# 5. Summary

## M&S plays a central role in propellant development

- used to identify target compounds, characterize synthesis routes and viable intermediates, verify successful synthesis

- prediction of bulk properties, including phase transitions, densities, thermal conductivities

- QSPR is useful tool for characterizing bulk properties, including toxicities

## Future directions(?)

- Atomic-level modeling of processes affecting sensitivities (esp. for ionic materials)

- Models for aging and surveillance in support of strategic sustainment

# 6. Backup Slides

# 3. Parallel Algorithms in GAMESS

**GAMESS is one of three codes ported to scalable hardware platforms as part of PRSP's CHSSI project.**

| Calc. type\Wavefunction type | RHF | ROHF | UHF | GVB | MCSCF |
|---|---|---|---|---|---|
| Energy | CDP | CDP | CDP | CDP | CDP● |
| Gradient | CDP | CDP | CDP | CDP | CDP● |
| Numerical Hessian | CDP | CDP | CDP | CDP | CDP● |
| Analytic Hessian | CDP | CDP | - | CDP | CDP |
| CI energy | CDP● | CDP● | n/a | CDP | CDP |
| CI gradient | CD | - | n/a | - | - |
| MP2 energy | CDP● | CDP● | CDP● | - | CP● |
| MP2 gradient | CDP● | - | CDP● | - | - |
| DFT Energy | CDP● | CDP● | CDP● | - | - |
| DFT Gradient | CDP● | CDP● | CDP● | - | - |
| CC Energy | CD | - | - | - | - |